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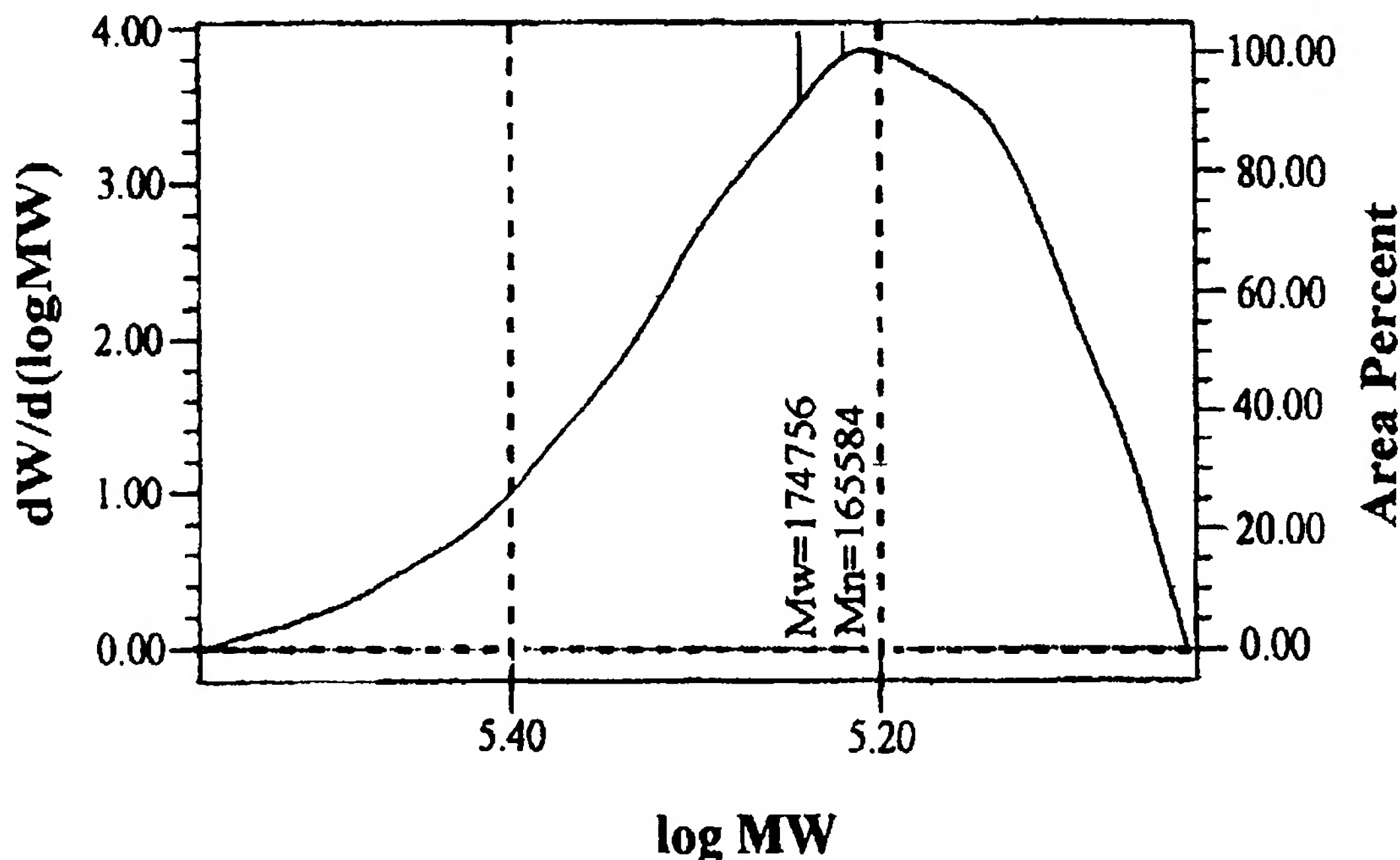
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(54) Title: **METHOD FOR MAKING POLYPYRROLE**



(57) Abstract: This invention is related to method for manufacturing soluble polypyrrole. Soluble polypyrrole can be obtained by the method in that pyrrole monomer and oxidant are added in solution having sulfosuccinic acid or its salt as dopant and reaction of the solution are polymerized and then vacuum dried.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TITLE OF INVENTION

METHOD FOR MAKING POLYPYRROLE

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TECHICAL FIELD

The present invention relates to the making method for variety polypyrrole which having a superior in solubility with organic solvent and thus able to be cast into films and solution-sprayed into coatings. Also, the present invention is
10 concerned with a process for preparing soluble, electroconductive polypyrrole by polymerizing pyrrole monomers in an aqueous solution in the presence of dodecylbenzene sulfonic acid (DBSA).

BACKGROUND ART

15

Since polypyrrole is high in electroconductivity and stable in the air, it is useful for a plurality of purposes including electroconductive coating materials and paints, electrode materials for batteries, semiconductor parts, electrolytes for solid electrolytic capacitors, solar cells utilizing solar energy into electricity and so on.
20 Accordingly, extensive research has recently been directed to the synthesis and applications of polypyrrole.

However, there are many limitations in its practical processing and application since the strong intermolecular interaction of the heterocyclic planar structure of polypyrrole makes it virtually impossible not only to dissolve
25 polypyrrole in any solvent, but also to melt it.

Polypyrrole can be easily synthesized by electrochemical or chemical polymerization techniques.

Films of polypyrrole uniform and superior in mechanical properties can be obtained by electrochemical polymerization techniques. In these techniques, correspondingly large electrodes are necessary to obtain a polypyrrole film with a large area. In addition, it is difficult to synthesize uniformly thick films by electrochemical polymerization techniques. Further, electrochemically synthesized polypyrrole films always have bumpy (shaped like bunches of grapes) surfaces (FIG. 1A), making it difficult to control electric and electronic functions when the polypyrrole films are used as electrode materials of micro-electric devices because the distances between the electrodes are different and thus, an oversupply of current passes in certain portions.

For chemical polymerization techniques the polypyrrole is obtained as powder which is insoluble so that it alone cannot be formed into films. Polymerization of pyrrole monomer through chemical oxidation is generally accomplished by the addition of a persulfate oxidant and an acid serving as a dopant, resulting in a polypyrrole doped with the acid anion. It is also reported that a powder of polypyrrole is obtained by using FeCl_3 as an oxidant and 2-naphthalene sulfonic acid or p-toluene sulfonic acid as a dopant. However, the powder obtained was not dissolved in any organic solvent.

Extensive studies were made to allow processability to polypyrrole. Most of them proceed toward weakening intermolecular interaction through modifications of pyrrole monomer, so as to give the resulting polypyrrole solubility. For example, a successful example of the solubility of polypyrrole is reported in J. Chem. Soc., Chem. Commun, 11, 725, 1989), which is accomplished by attaching an alkyl group with a long chain, such as octyl, to pyrrole monomer. However, the pyrrole derivative is difficult to synthesize and costs too much compared with non-substituted pyrrole. Besides, the modified polypyrrole is very poor in electroconductivity and examples of its actual applications are indeed rare.

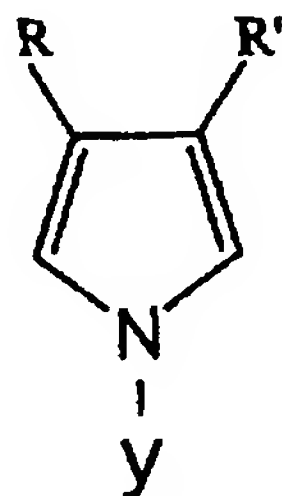
DISCLOSURE OF INVENTION

It is an object of the present invention to provide a method for making soluble polypyrrole to solve the above described problems

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In accordance with one aspect of the present invention, solute pyrrole monomer according to general expression (I) and sulfosuccinic acid or its salt for dopant added oxidizer to polymerize and vacuum dried to acquit compound according to expression (III)

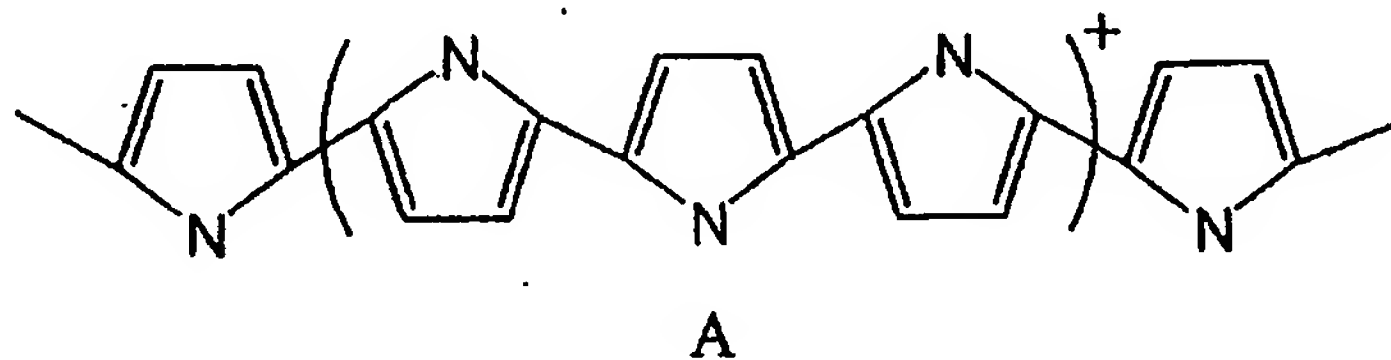
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general expression (I)

(R,R' and y are hydrogen, one to twenty of carbon which are alkyl, isoalkyl, alkoxy, alkoxyalkyl, alkylsulphonyl, alkoxysulphonyl, alkylcabonyl, alkoxycabonyl, alkylsilane, alkoxysilane, arylsulphonyl, alkenyl)

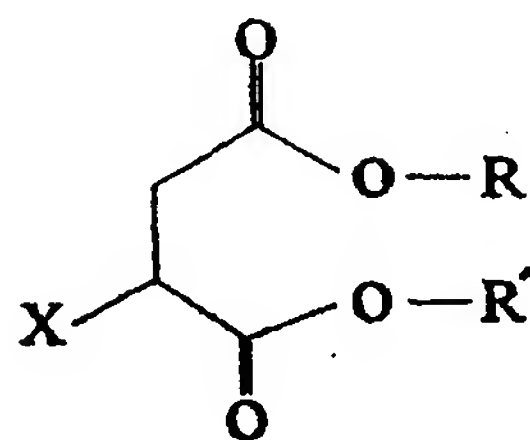
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general expression (III)

(R,R' and y are the same above mentioned, \bar{A} is anion of dealkylsulphosuccinate)

Dopant is a compound to have general expression (II).



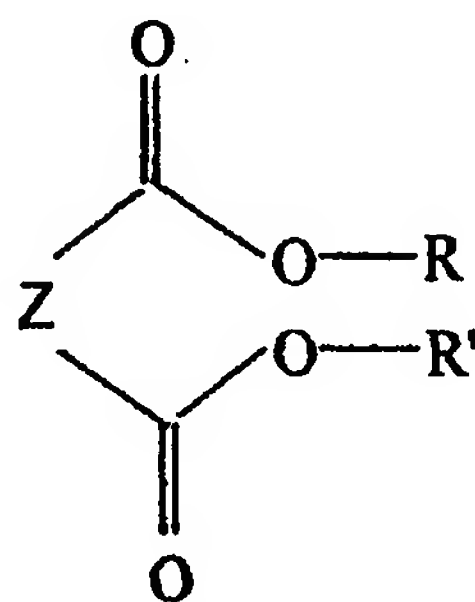
general expression (II)

5

(R and R' are the same above mentioned, X is sulphonic acid, carboxylic acid, phosphonic acid or its salt)

Dopant is a compound of general expression (V) or its salt.

10



general expression (V)

Dopant is mixed with one of aromatic sulphonic acid group which consisting benzene sulphonic acid, toluene sulphonic acid, sulphosalicylic acid, naphthalene sulphonic acid, naphthalene disulphonic acid, naphthol amino disulphonic acid, anthraxquinone sulphonic acid anthraxquinone-disulphonic acid or said group's salt.

Dopant is mixed with one of aromatic carboxylic acid group which consisting benzene carboxylic acid, toluene carboxylic acid, naphthalene carboxylic acid, naphthalene-disulphonic acid, anthraxquinone carboxylic acid or said group's salt.

5 Dopant is mixed with one of aromatic phosphonic acid group and aromatic phosphonic acid which consisting benzene phosphonic acid, toluene phosphonic acid, naphthalene phosphonic acid, anthraxquinone phosphonic acid, anthraxquinone-diphosphonic acid, benzene phosphonic acid, toluene phosphonic acid, naphthalene phosphonic acid, anthraxquinone phosphonic acid,
10 anthraxquinone-diphosphonic acid or said group's salt.

Oxidizer which mixing 1:0 to 0:1 in mole fraction with ammonium persulfate and one of a group which consisting ammonium iron sulfate, iron sulfate, iron perchloric acid, potassium peroxide, dipotassium chromate, para toluene iron sulfate.

15 It is composition that soluble polypyrrole in organic solvent which consisting water, alcohol, chloroform, dichloromethane, acetonitrile, formic acid etc. or mixed said organic solvent.

It is composition that said soluble polypyrrole under response temperature in -30°C to 60°C .

20 It is composition that said soluble polypyrrole under response time in 30 minute to 90 hour.

Mole fraction for said oxidizer and said pyrrole monomer is 1: 10 to 2:1.

25

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 shows the graph to illustrate measurement result of polypyrrole

molecular weight in accordance with the present invention.

FIG. 2 shows the graph to illustrate FT-IR spectrum measurement result of polypyrrole powder in accordance with the present invention.

FIG. 3 shows the graph to illustrate UV/Vis-NIR spectrum for polypyrrole solution to melt polypyrrole in accordance with the present invention with alcohol solvent.

FIG. 4 shows the graph to illustrate UV/Vis-NIR spectrum for polypyrrole solution to melt polypyrrole in accordance with the present invention with organic solvent.

BEST MODE FOR CARRYING OUT THE INVENTION

The polypyrrole according to the present invention is soluble in an organic solvent, and thus it is capable of being spray-coated by virtue of its superior solubility, and is capable of being processed into conductive composites.

The soluble polypyrrole according to the present invention is capable of being cast into films having a smooth surface. Herein, the term "soluble polypyrrole" means that it can be formed into films which can have any desirable thickness and size.

The present invention provides polypyrrole represented as the following structural formula II: ##STR6##

In the present polypyrrole, an anion, denoted by A.sup.-, which results from the dissociation of dodecylbenzene sulfonic acid, acts as a dopant which is doped in the polymer, rendering electroconductivity to it. Since this dopant is located between the molecules of polypyrrole and has a molecular weight of about 5 times as large as a pyrrole monomer, it prevents the polypyrrole molecules from coming

into direct contact with each other. Thus, the dopant greatly reduces the intermolecular interaction of polypyrrole, resulting in large improvements in the solubility of the polypyrrole. It is known to those knowledgeable in the art that one anion is doped per 3 or 4 pyrrole repeating units.

5 Powders of the polypyrrole according to the present invention are dissolved in weakly polar organic solvents such as dichloromethane and m-cresol and polar organic solvents such as tetrahydrofuran (THF) and dimethylformamide (DMF). Also, they could be dissolved even in chloroform provided that dodecylbenzene sulfonic acid is added at an amount of 100 to 200 weight % based on the total
10 weight of the polypyrrole.

 Gel permeation chromatography (GPC), which is generally used to measure molecular weights of polymers, is not effective for doped conductive polymers which are in an oxidation state. Further, because K and a values, necessary for the Mark-Houwink equation, are not known for polypyrrole, its molecular weight
15 cannot be determined by measurement of inherent viscosity.

 But, the intrinsic viscosity of a m-cresol solution dissolving the polypyrrole according to the present invention is about from 0.07 dl/g to 0.3 dl/g at 30.degree. C. which is lower than that of soluble polyaniline, 0.18-2.62 dl/g as reported in Polymer 34, 3139 (1993) by Y. Cao and P. Smith.

20 Such low intrinsic viscosity means that the molecular weight of the soluble polypyrrole according to the present invention is not so large.

 The soluble polypyrrole of the present invention is prepared by polymerizing pyrrole monomer in the presence of a persulfate oxidant. In more
25 detail, to a solution of dodecylbenzene sulfonic acid and pyrrole monomer in distilled water, persulfate oxidant is slowly added with stirring in an incubator at a temperature of -5.degree. to 20.degree. C. for 24 hrs at the constant temperature.

Thereafter, methanol is added to stop the polymerization. The synthesized powdery polypyrrole was filtered, washed many times with distilled water and methanol.

It is preferred that the concentration of dodecylbenzene sulfonic acid upon polymerization of pyrrole is on the order of 0.1 to 1.0 mole based on the moles of pyrrole monomer. A concentration departing from the range results in undesirable solubility of polypyrrole.

As the persulfate oxidant, potassium persulfate or ammonium persulfate is used in the present invention with a preference to ammonium persulfate. The persulfate oxidant is added preferably at 0.1-0.5 mole per unit mole of pyrrole monomer and more preferably at 0.1-0.2 mole per unit mole of pyrrole monomer. As the concentration increases within this range, the conductivity of the film obtained by casting and the production yield increase while the solubility thereof decreases. If the mole ratio of the persulfate oxidant to pyrrole monomer is above 0.5, the solubility markedly decreases. On the other hand, if the mole ratio is less than 0.1, the conductivity of a cast film drops into less than 10^{-6} S/cm while the solubility is improved.

In contrast with the electrochemically polymerized polypyrrole film having a bumpy surface as shown in FIG. 1A, the polypyrrole prepared according to the method of the present invention, when a film is formed by casting a solution that the present polypyrrole is dissolved in an organic solvent, has a smooth surface without any bumps, as shown in FIG. 1B. From this fact, it is apparent that a smooth surface with a good electroconductivity can be obtained when the soluble electroconductive polypyrrole prepared according to the present invention is coated on some surface. As a result, the polypyrrole of the present invention can be more extensively used. For example, the polypyrrole film according to the present invention is completely free of surface bumps, which are seriously problematic to electrochemically polymerized polypyrrole films used as a pair of electrodes with a

very small gap, and thus, can be used as excellent electrode materials that do not have differences in the distances between the electrodes.

With reference to FIG. 2, there are shown FT-Raman spectra for a film obtained by casting the present polypyrrole solution and an electrochemically polymerized polypyrrole film. These spectra are completely the same, showing that the chemical structure of the soluble polypyrrole prepared according to the present invention is identical to that of electrochemically polymerized polypyrrole.

It is believed that one reason why the present polypyrrole is different from the electrochemically synthesized polypyrrole in solubility in spite of an identical chemical structure is that they are different from each other in molecular weight and/or crosslink density. As apparent from the solubility, the present method scarcely generates intermolecular crosslinks in polypyrrole, compared with the electrochemical polymerization method. In accordance with the present invention, the molecular weight of polypyrrole can be controlled by the concentration of the oxidant. In contrast, the polypyrrole obtained by electrochemical polymerization or chemical polymerization does not allow its molecular weight to be measured because of its absolute insolubility.

By controlling the reaction conditions including reaction temperature and concentrations of dodecylbenzene sulfonic acid and a persulfate oxidant, the solubility in organic solvents of the soluble polypyrrole obtained by the method of the present invention and the conductivity thereof can be adjusted.

The soluble polypyrrole according to the present invention is capable of being cast into films having a smooth surface.

As the surface of a conductive material is smoother, the electromagnetic functions thereof become more uniform, which allows micro-devices to be formed with high reproductivity.

In addition, when being blended with other polymeric materials in order to

improve adhesiveness or strength, the conductive material with a smoother surface can be easily formed to have superior electric functions by, example, coating it on glass or polymeric film. In this case, it is possible to obtain transparent electrode plates equivalent to a transparent ITO glass plate by controlling the thickness of
5 the polypyrrole coating.

In addition, a significance of the soluble polypyrrole according to the present invention is that it can be solution-blended with various general-purpose polymers capable of being dissolved in organic solvents, such as polystyrene (PS), amorphous nylon and poly(methylmethacrylate) (PMMA), to form conductive
10 films with good mechanical properties.

As explained above, the electroconductive polymers obtained by the method of the present invention are easily dissolved in organic solvents, so that they show superior processability, which allows them to be applied for a wide range of uses including electroconductive coating materials and paints, electrode
15 materials for batteries, semiconductor parts, electrolytes for solid electrolytic capacitors, solar cells utilizing solar energy as electricity and so on.

A better understanding of the present invention may be obtained in light of the following examples which are set forth to illustrate, and are not to be construed to limit, the present invention.

20

EXAMPLE I

24.3 g (0.0745 mol) of dodecylbenzene sulfonic acid was dissolved in 300 ml of deionized water and the solution was poured into a reactor, which was then
25 placed in an incubator at a temperature of 5.degree. C. 10 g (0.149 mol) of pyrrole monomer which was dried with calcium halide and distilled under reduced pressure was added to the resulting solution which was then vigorously stirred for

20 min. with a mechanical stirrer. To this solution, 3.65 g (0.016 mol) of ammonium persulfate solution in 100 ml of deionized water was added over 5 min. and reacted for 16 hrs. with stirring. The addition of 300 ml of methanol stopped the reaction and the solution was filtered to obtain a fine polypyrrole powder. The
5 polypyrrole powder was washed with excess deionized water and methanol and filtered to give pure polypyrrole: yield 20.8%.

The solubilities of the polypyrrole in m-cresol, chloroform, THF and DMF, each, were examined and the results are given as shown in Table 1.

Using a thin disc-like specimen made by compressing the pure polypyrrole
10 powder and a film (thickness: 100 .mu.m) made by casting a polypyrrole solution in chloroform, voltages were detected under a constant current by the four probe method, to examine thoes conductivities, and the results are given as shown in Table 2.

15 As indicated in Table 1, the polypyrrole prepared according to the present invention is well dissolved in m-cresol, THF and DMF but not in chloroform. In the latter case, when dodesylbenzene sulfonic acid was further added at an amount of 50 weight % based on the weight of the polypyrrole, the polypyrrole was dissolved very well.

20

EXAMPLE II

Pure polypyrrole powder was prepared in a similar manner to that of Example I, except that 7.3 g (0.032 mol) of ammonium persulfate was used. Yield
25 63.6%.

The results of the analyses for solubility and conductivity are given as

shown in Tables 1 and 2, respectively.

As indicated in Table 1, the polypyrrole prepared in this example was superior in solubility in m-cresol, THF and DMF to the polymer prepared in Example 1 but not dissolved in chloroform. In the latter case, when
5 dodesylbenzene sulfonic acid was further added at an amount of 50 weight percent based on the weight of the polypyrrole, the polypyrrole dissolved very well. As shown in Table 2, the polypyrrole film of this example has about 700 times as high a conductivity as does that of Example I. In the case of the compressed powder, the conductivity of Example II is about 360 times as high as that of Example I.
10 Consequently, the conductivities of the polypyrrole film and the powder of Example II are much improved relative to those of the polypyrrole film and the powder of Example I.

COMPARATIVE EXAMPLE I

15

Pure polypyrrole powder was prepared in a similar manner to that of Example I, except that 18.25 g (0.080 mol) of ammonium persulfate was used. Yield 87.6%.

The results of the analyses for solubility and conductivity are given as
20 shown in Tables 1 and 2, respectively.

Although its conductivity is 14.4 S/cm, a high value when compressed, the powder is of low solubility in the organic solvents. Thus, a solution capable of being casted into films could not be obtained by using the solvents.

25

TABLE 1

Solubility of the Soluble Polypyrrole

Solvent				
Example No.				
	m-Cresol	THF	DMF	Chloroform
5	Example I CS	CS	CS	PS (CS*)
	Example II			
	CS	CS	CS	PS (CS*)
	C. Example I			
	PS	IS	IS	IS
10	note:			
	PS: partially soluble,			
	CS: completely soluble,			
	IS: insoluble,			
15	CS*: completely soluble after addition of a certain amount of DBSA			

TABLE 2

Conductivity of Soluble Polypyrrole Powder and Film from Chloroform Sol'n				
Conductivity (s/cm)				
Example No. Compressed Powder				
	Film			
20				
25	Example I	2.97 .times. 10.sup.-3		
		1.25 .times. 10.sup.-2		
	Example II	1.10	8.90	

C. Example I

14.35

Impossible Casting

5

EXAMPLE III

The polypyrrole obtained in Example II in combination with polymethy(methacrylate), sold by Polyscience, Inc., under the designation of "IV: 1.3", was dissolved in various concentration ratios in chloroform with dodecylbenzene sulfonic acid, to give solution blends, which were then cast into films. The conductivities of these films were measured by the four probe method. The results are shown in FIG. 3.

As plotted in FIG. 3, when the content of the polypyrrole is 16.7, 28.6, 37.5 and 50 weight %, the conductivity is 1.5×10^{-1} , 6.6×10^{-1} , 7.6×10^{-1} and 1.6 S/cm, respectively, which indicates that a higher content of polypyrrole results in a higher conductivity. Besides, up to 50 weight % of polypyrrole still resulted in a film with high mechanical strengths.

Other features, advantages and embodiments of the present invention disclosed herein will be readily apparent to those exercising ordinary skill in the art after reading the foregoing disclosures. In this regard, while specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

25

EXAMPLE IV

The mechanical properties of a film made by casting the polypyrrole of Example II, a conventional polypyrrole (polypyrrole-DS) and a polyaniline are given as shown in the following Table 3.

TABLE 3

5

Polypyrrole-			
		Polypyrrole-	
		unstretched*.sup.3	
Mechanical Property			
10	DBSA*.sup.1		
	DS*.sup.2 Polyaniline		
<hr/>			
	Tensile Strength at Break		
	17.0	68.5	54.4
15	(MPa)		
	Elastic Modulus (MPa)		
	1945	--	--
	Elongation at Break (MPa)		
	0.9	7.7	--
20	<hr/>		
	*.sup.1 : dodecylbenzene sulfonic acid,		
	*.sup.2 : dodecyl sulfate ion, J. M. Ko, H. W. Rhee and C. Y. Kim,		
	Makromol. Chem. Macromol. Symp., 33, 353-359 (1990)		
	*.sup.3 : "Conjugated Polymers and Related Materials", ed. W. R.		
25	Salaneck		
	I. Lundstrom, B. Ranby, 1993, 92		

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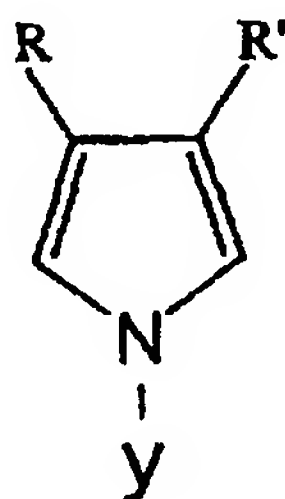
As apparent from Table 3, the polypyrrole according to the present invention is comparable in mechanical properties with electrochemically synthesized polypyrrole films and cast polyaniline films.

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Claims

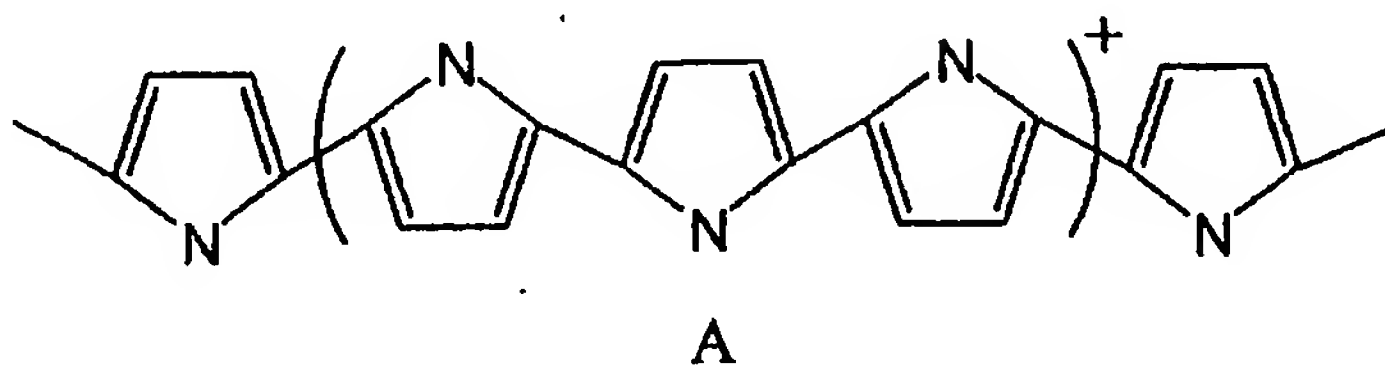
What is claimed is:

1. A method for making soluble polypyrrole comprising a solution which
 5 solute pyrrole monomer according to general expression (I) and sulfosuccinic acid
 or its salt for dopant added oxidizer to polymerize and vacuum dried to acquit
 compound according to expression (III)



general expression (I)

- 10 (R,R' and y each of them are hydrogen, one to twenty of carbon which are
 alkyl, isoalkyl, alkoxy, alkoxyalkyl, alkylsulphonyl, alkoxy sulphonyl, alkylcabonyl,
 alkoxy cabonyl, alkylsilane, alkoxy silane, arylsulphonyl, alkenyl)



general expression (III)

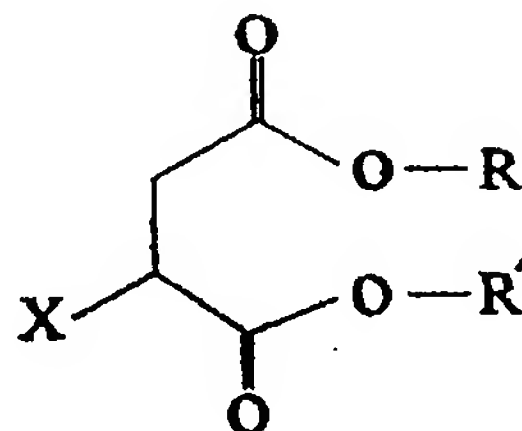
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(R,R' and y are the same above mentioned, \bar{A} is anion of
 dealkylsulphosuccinate)

2. The method in accordance with claim 1, wherein said polypyrrole has an

average molecular weight in 2,000 to 500,000.

3. The method in accordance with claim 1, wherein said dopant is a compound to have general expression (II).



general expression (II)

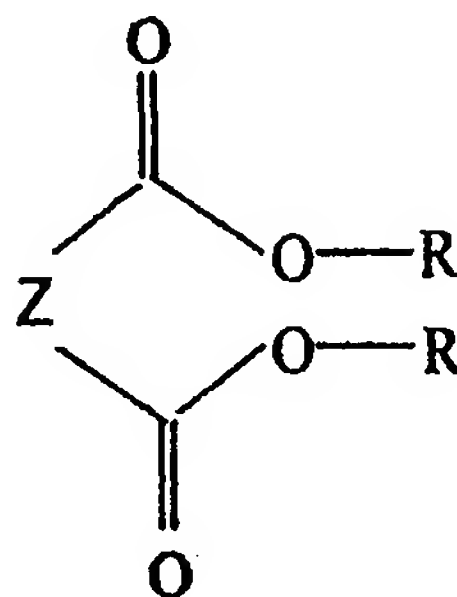
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(R and R' are the same above mentioned, X is sulphonic acid, carboxylic acid, phosphonic acid or its salt)

10 4. The method in accordance with claim 3, wherein said dopant is de-(2-ethylhexyl) sulphosuccinic acid or its salt.

5. A method in accordance with claim 1, wherein said dopant is a compound of general expression (V) or its salt.

15



general expression (V)

6. The method in accordance with any one of claim 3 to claim 5, wherein said salt is sodium, potassium, lithium, calcium, magnesium.

7. The method in accordance with claim 3, wherein said dopant is mixed with one of aromatic sulphonic acid group which consisting benzene sulphonic acid, toluene sulphonic acid, sulphosalicylic acid, naphthalene sulphonic acid, naphthalene disulphonic acid, naphthol amino disulphonic acid, anthraxquinone sulphonic acid anthraxquinone-disulphonic acid or said group's salt.

8. The method in accordance with claim 3, wherein said dopant is mixed with one of aromatic carboxylic acid group which consisting benzene carboxylic acid, toluene carboxylic acid, naphthalene carboxylic acid, naphthalene-disulphonic acid, anthraxquinone carboxylic acid or said group's salt.

9. The method in accordance with claim 3, wherein said dopant is mixed with one of aromatic phosphonic acid group and aromatic phospholic acid which consisting benzene phosphonic acid, toluene phosphonic acid, naphthalene phosphonic acid, anthraxquinone phosphonic acid, anthraxquinone-diphosphonic acid, benzene phospholic acid, toluene phospholic acid, naphthalene phospholic acid, anthraxquinone phospholic acid, anthraxquinone-diphospholic acid or said group's salt.

10. The method in accordance with claim 1, wherein said oxidizer which mixing 1:0 to 0:1 in mole fraction with ammonium persulfate and one of a group which consisting ammonium iron sulfate, iron sulfate, iron perchloric acid, potassium peroxide, dipotassium chromate, para toluene iron sulfate.

11. The method in accordance with claim 1, it is composition that soluble

polypyrrole in organic solvent which consisting water, alcohol, chloroform, dichloromethane, acetonitrile, formic acid etc. or mixed said organic solvent.

12. The method in accordance with claim 1, it is composition that said soluble polypyrrole under response temperature in -30°C to 60°C.

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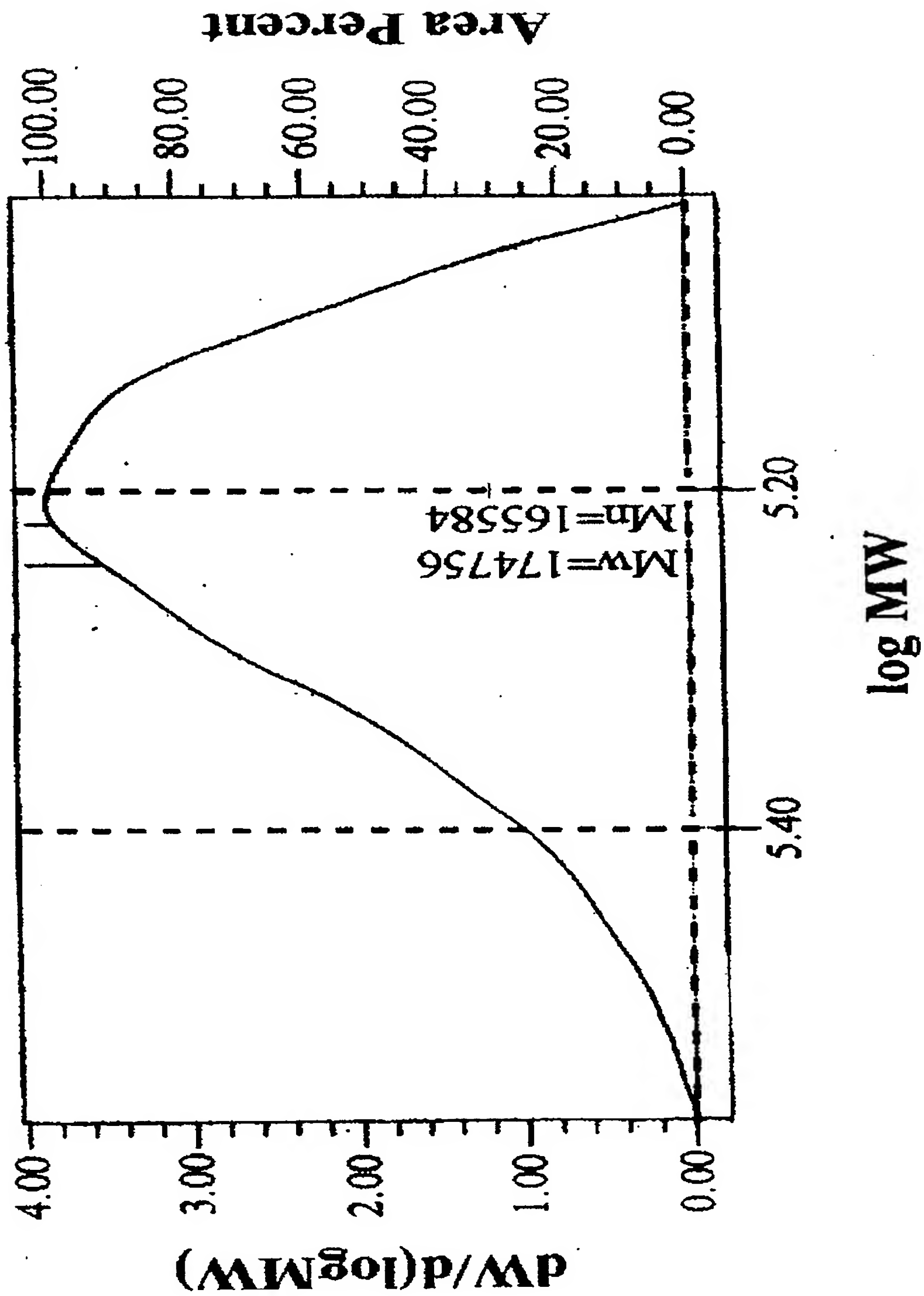
13. The method in accordance with claim 1, it is composition that said soluble polypyrrole under response time in 30 minute to 90 hour.

14 The method in accordance with claim 1, mole fraction for said oxidizer
10 and said pyrrole monomer is 1: 10 to 2:1.

15. The method in accordance with claim 1, wherein said oxidizer is adding during 5 seconds to 2 hour.

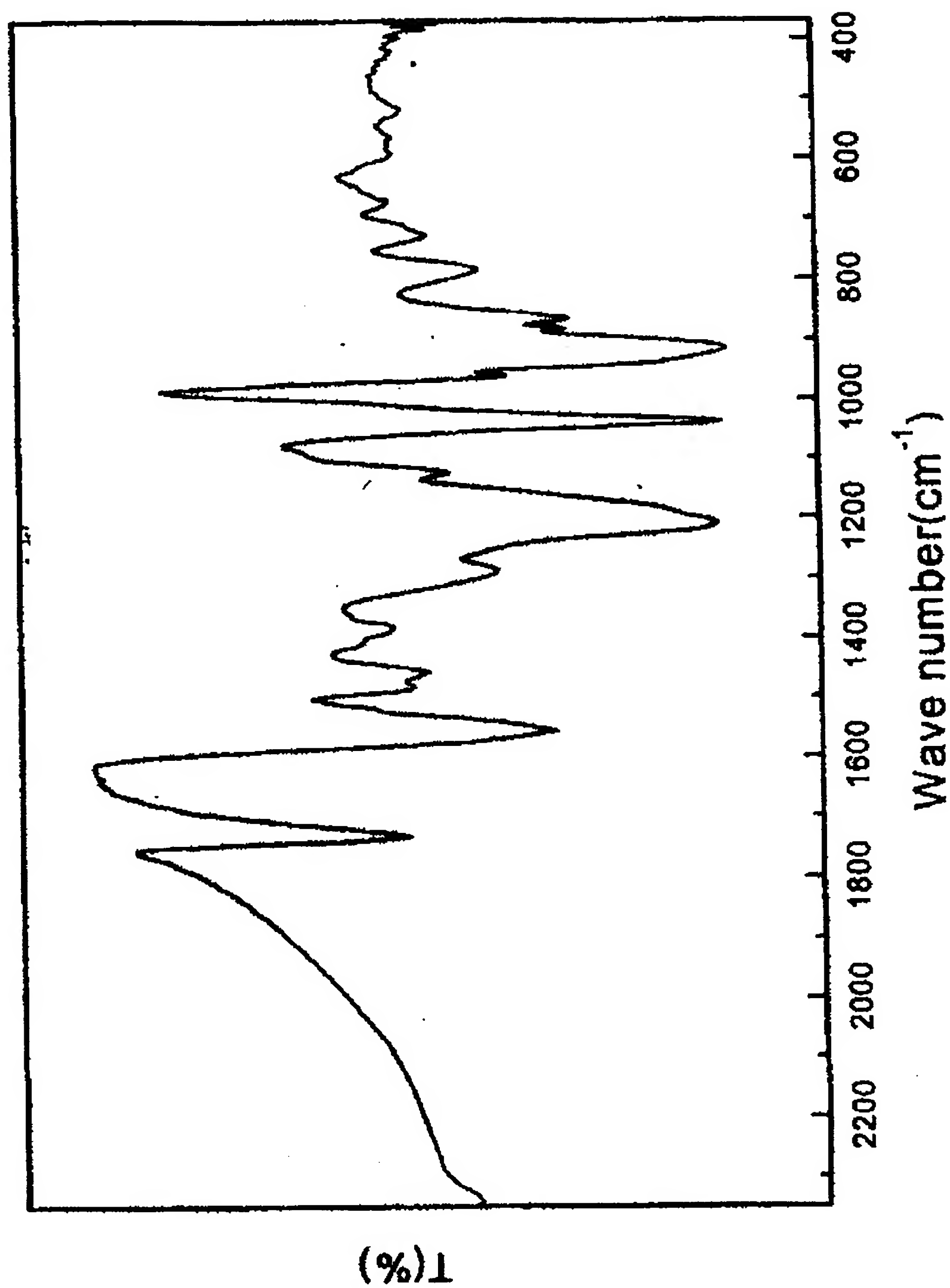
15 16. The method in accordance with claim 1, wherein said oxidizer is adding at most 1 time to 5 times.

FIG. 1



2/4

FIG.2



3/4

FIG. 3

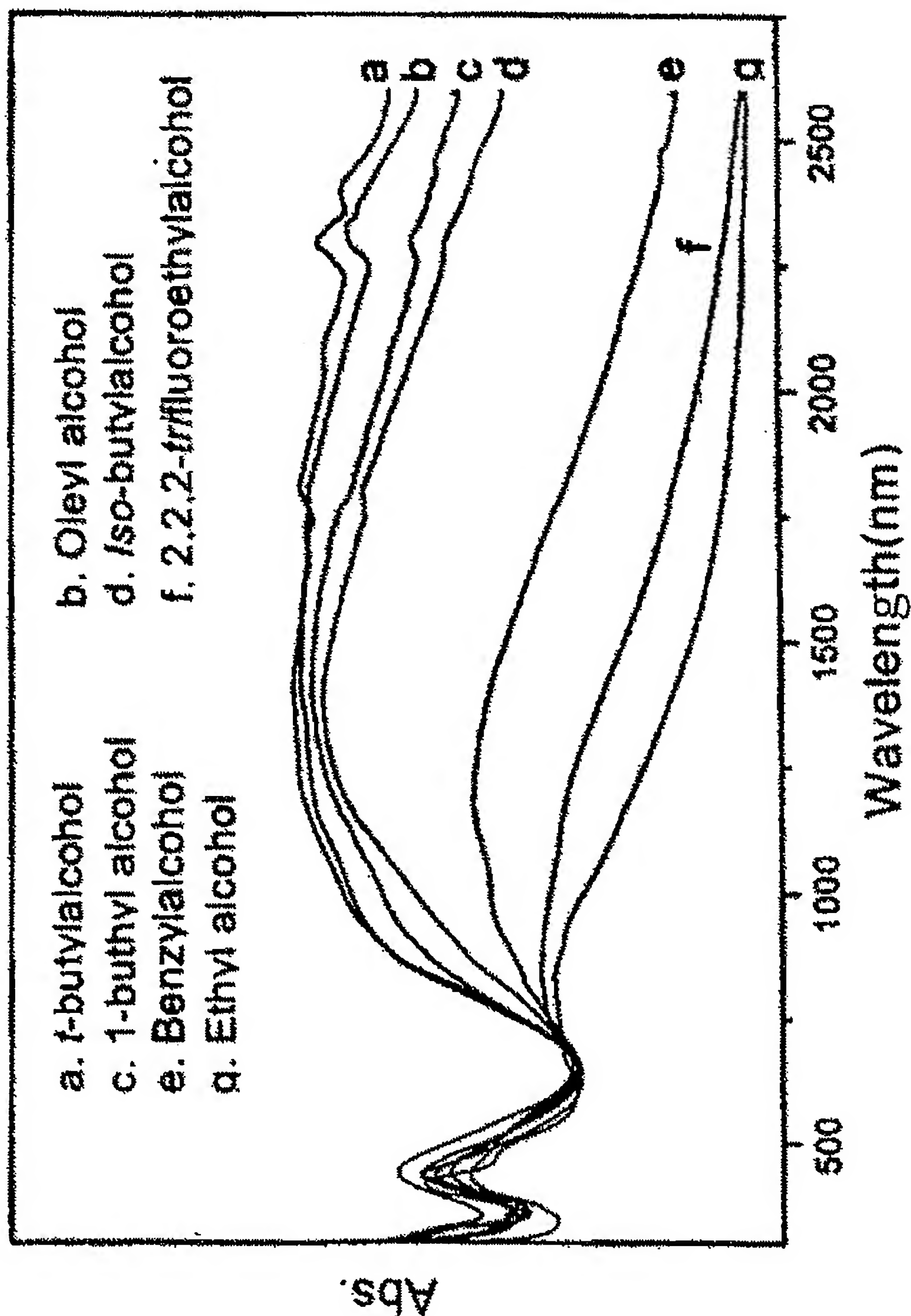
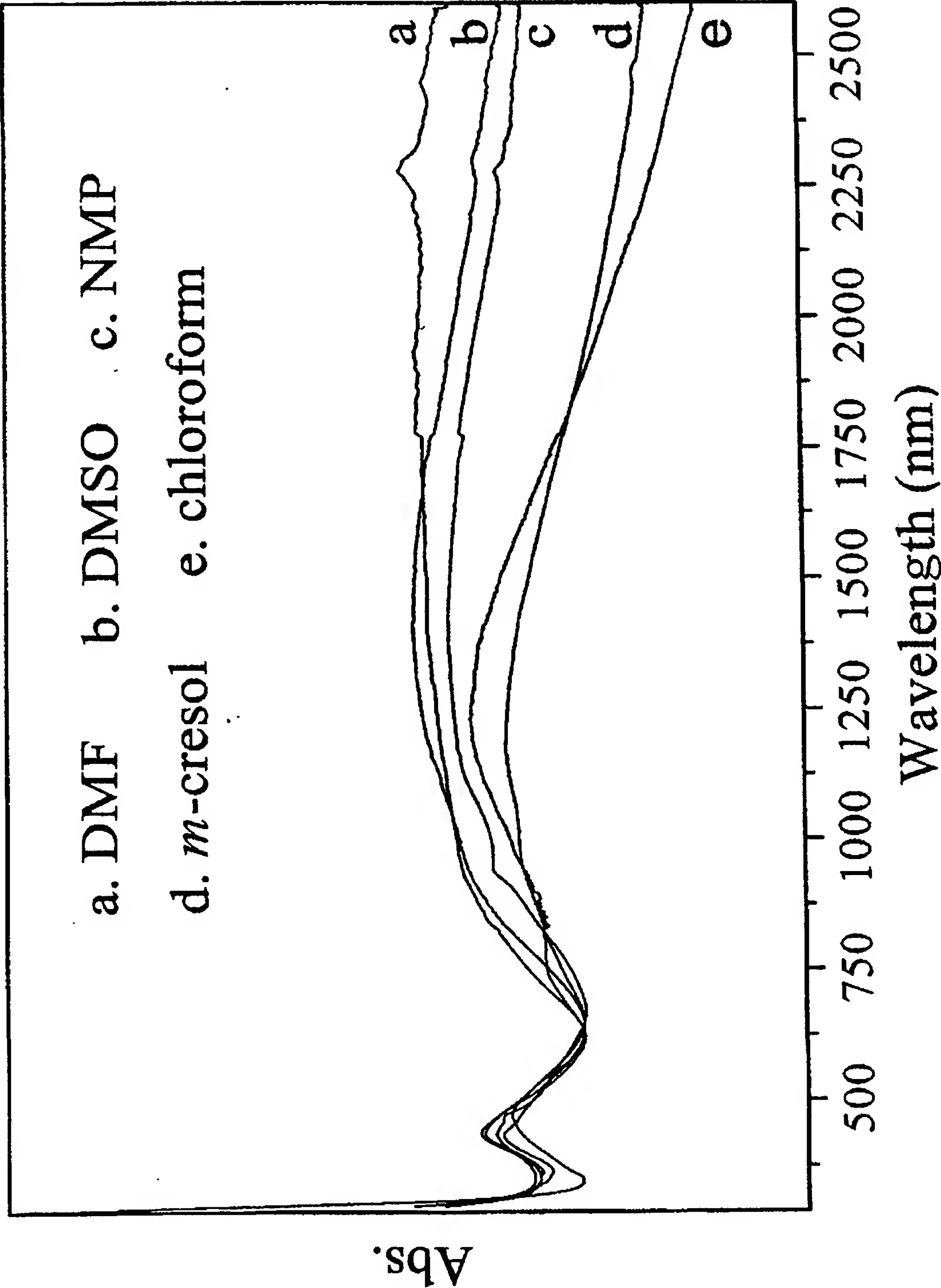


FIG.4



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR01/00982**A. CLASSIFICATION OF SUBJECT MATTER****IPC7 C08G 61/12**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G 61/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

KR

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PAJ, EPO-WEB, KIPO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,795,953 A(1998.08.18) see the whole document	1-16
X	KR 1999-0073157 A(1999.10.05) see the whole document	1-16
X	KR 2000-0001140 A(2000.01.15) see the whole document	1-16
A	JP 03-122115 A(1991.05.24) see the whole document -----	1-16

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

17 AUGUST 2001 (17.08.2001)

Date of mailing of the international search report

20 AUGUST 2001 (20.08.2001)

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Telephone No. 82-42-481-5549



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR01/00982

Patent document
cited in search report

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None

----- End of Documents -----